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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: CONDUCTING POLYMER FILMS		
(57) Abstract The invention relates to a conducting polymer film comprising a polymer, such as poly(aniline) and/or polypyrrole, and an organosulphonate and/or organophosphonate counterion such as represented by the formula: $R(X)_n$ where R = a C ₁ to C ₁₀ straight, branched cyclic or polycyclic alkyl or ketoalkyl group or organometallic group, X = -SO ₃ ⁻ or -PO ₃ ²⁻ , n = 1-4. The invention also provides a method of producing the conducting polymer film and a method of producing a thin conductive polymer film.		

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CONDUCTING POLYMER FILMS

The present application relates to conducting polymer films in particular for use with sensor arrays, and to an improved method of allowing such polymers to bridge the gap between two electrodes making up a sensor.

5 Sensors comprising a substrate and an electrochemically deposited polymer region are known in the art. The signals from such sensors can be used to discriminate, for example between different types of beverage (such as coffee and beer) and foodstuffs and identify malodours and taints. Each sensor is made by producing a pattern of electrodes on an insulating substrate, for example by physically
10 evaporating 99.99% pure gold onto a silicon substrate and etching an electrode pattern by conventional ultra-violet lithography.

The polymer may be put onto the electrode by dipping the tile into a bath of electrolyte, polymer and solvent, and applying a potential between the gold layer
15 and a reference electrode in a three electrode configuration or between the gold layer and a counter electrode in a two electrode configuration, resulting in polymer deposition to form a sensor. Alternatively, the polymer may be deposited using the hanging drop deposition technique disclosed in the applicant's co-pending International patent application no. PCT/GB95/00090 which is incorporated herein
20 by reference. Electrochemical material deposited by such a technique may also be used for friction reduction and other uses described in the reference.

Several different conducting polymers are known in the art. For example, the use of poly(aniline) films grown with sulphate counterions is known but these films were found to be inherently unstable. Thus the base-line resistance gradually increased with time at a significant rate of 1-10% per week. Also, the films were found to be very sensitive to humidity and temperature fluctuations. Odour sensors using such films thus did not produce responses which could be reliably interpreted and the practical use of the films was thus limited. The inventors have however unexpectedly found that the use of organosulphonates as counterions to polymers such as poly(aniline) or poly(pyrrole) produce conducting polymers with improved properties over polymers of the prior art, in particular providing stable base line resistance and low sensitivity to humidity and temperature fluctuations.

Conventionally the gap between electrodes has to be limited to around 5-25 microns to ensure that sufficient conducting polymer is deposited to bridge the gap. In a second aspect of the invention the inventors have identified a method of growing thin films of polymer along a substrate, which allows gaps between the electrodes of about 40-100 microns to be used, resulting in greater electrode sensitivity. This technique is based upon the treatment of glass substrates with n-alkylsilane discussed by Nishizawa M *et al* (J. Electrochem.Soc., Vol. 140. No. 6, (1993), pages 1650-1655). This technique was used to produce an enzymatic sensor operating in solution. It will be appreciated that the known use of the technique is quite different from its use in friction reduction layers and gas sensors.

Viewed from a first aspect, the invention provides a conducting polymer film comprising a polymer and an organosulphonate and/or an organophosphonate counterion. The polymer preferably is poly(aniline) or poly(pyrrole). The counterion may be represented by the general formula:



where:

R = a C₁ to C₁₀ straight, branched cyclic or polycyclic, alkyl or ketoalkyl group, or an organometallic group.

X = -SO₃⁻ or -PO₃²⁻

n = 1-4.

Preferably R is a C₁ to C₁₀ straight chain alkyl, an isomer of camphor or copper II phthalocyanine.

Most preferred combinations of polymer and counterion are:

Poly(aniline) with butanesulphonate, pentanesulphonate, hexanesulphonate, heptanesulphonate, octanesulphonate, nonanesulphonate, decanesulphonate, (1R)-(-)-10-camphorsulphonate, (1S)-(+)-10-camphorsulphonate, or (±)-10-camphorsulphonate counterions.

Poly(pyrrole) such as poly(N-methylpyrrole) with methanephosphonate, ethanephosphonate, butanephosphonate, decanephosphonate. (1R)-(-)-10 camphorsulphonate, (1S)-(+)-10- camphorsulphonate, or (\pm)-10- camphorsulphonate or copper (II) phthalocyaninetetrasulphonate counterions.

5

The polymers may be deposited onto gold, platinum, carbon, tin dioxide, copper or doped silicon electrodes.

The conductive polymer films of the invention may be used in sensing devices or
10 for friction reduction.

The invention also provides a method of deposition of a conducting polymer film according to the first aspect of the invention.

15

The deposition of polymer films such as poly (aniline) films, with counterions, such as alkane sulphonate, can be improved by deposition above room temperature, preferably above 30°C, above 40°C, above 50°C or most preferably between 50°C and 60°C, especially 50°C to 55°C. Reproducible thin films have
20 been found by the inventors to be producible by growing across at a fixed potential of +0.9 V vs. SCE (Standard Calomel Electrode). The thickness of the films may be varied by changing the growth time at, for example, 0.9 V.

Preferably, the films are subsequently heat treated at a higher temperature, at for example about 80°C. for, for example, 24 hours in air. This leads to an increase in the film resistance and can be used to stabilise the response of the sensor.

5 There are a number of advantages deriving from the invention. Regarding the poly(aniline) films, these films have excellent frictional properties. In the sensing field, they have a higher resistance per square metre which makes it easier to interface them with an electronic circuit as the effects of lead resistance and Joule heating are reduced. The stability of the polymers is very good with little observed
10 base-line resistance drift. In this respect they are significantly superior to the prior poly(aniline) sulphate film. At the same time they are highly sensitive and therefore can sense accurately. They also have a thermal sensitivity which is much lower than the prior poly(aniline) sulphate films so that fluctuations in the ambient temperature are less critical. The poly(pyrrole) films are a new group of materials
15 for application in gas/vapour sensing and have different patterns of response from known sensors making them extremely useful for use in a multi-sensor array for detailed analysis. The poly(pyrrole) films have excellent frictional properties.

Viewed from a second aspect, the invention provides a method of
20 electrochemically producing a thin conductive polymer film on a substrate comprising silanizing the substrate. The substrate is preferably silicon, and the silanizing compound is preferably one or more silanes such as n-alkylsilanes, for

example octyltrichlorosilane. The conductive polymer deposited by this method may be a polymer according to the first aspect of the invention.

Embodiments of the invention will now be described by way of example and with reference to Tables 1 and 2 and Figs. 1 to 5. Fig. 3 is a plan view of a polymer film sensor of the invention. Table 1 summarises resistance data for polypyrrole films grown with different alkane phosphonate by potential step to a fixed growth potential (Eg). Table 2 summarises the values for certain parameters. Fig. 1 is a graph of resistance in air against polymer chain length; Fig. 2 is a graph of activation energy against chain length; Fig. 4 is a graph of friction co-efficient for poly(pyrrole) with different counterions; and, Fig. 5 is a graph of wear rate against friction co-efficient.

POLYMER PRODUCTION

Deposition

All polymer depositions were carried out using a conventional three electrode system comprising the substrate structure as a working electrode with a saturated calomel (SCE) reference electrode and a large area platinum gauze counter electrode. Each substrate was made from a silicon wafer. A 1 μ m layer of silicon dioxide was grown on the silicon wafer. A 10nm layer of titanium was then deposited followed by a 250nm layer of gold. Using ultra violet lithography the required electrode pattern was produced to result in the geometry shown in Fig. 3,

6/1

Dopant	Eg / V vs. SCE	time /s	concentration / mol dm ⁻³	R/Ohm
BPA	+0.8	360	0.1	5800+/-2900 (n=3)
PPA	+1.0	120	0.1	3910+/-550 (n=6)
HxPA	+1.0	120	0.1	855+/-283 (n=5)
HpPA	+1.0	360	0.05	238+/-162 (n=5)
OPA	+1.0	360	0.05	832+/-701 (n=4)
NPA	+1.0	360	0.05	987+/-880 (n=6)
DPA	+1.0	240	0.05	1300+/-900 (n=4)
UPA	+1.0	360	0.05	4820+/-3070 (n=5)

BPA butane phosphonic acid
 PPA pentane phosphonic acid
 HxPA hexane phosphonic acid
 HpPA heptane phosphonic acid
 OPA octane phosphonic acid
 NPA nonane phosphonic acid
 DPA decane phosphonic acid
 UPA undecane phosphonic acid

TABLE 2

Parameter	Units	Minimum	Typical	Maximum	Note:
Resistance in air ¹	Ω	10	100	10k	For 10 μm gap ⁷
Resistivity in air	$\Omega\Box$	1 k	10 k	1 M	Thin film
Resistance in odour ^{2,3}	%	± 0.1	± 1	± 10	Relative to air
Ohmic	%	-	< 2	-	± 1 V d.c. reference
Dielectric constant	-	-	8	-	d.c. to 100 kHz
Temp. coefficient of resistance	$^{\circ}\text{C}$	0	- 5	- 16	Measured over range of 0 to 100 $^{\circ}\text{C}$
Activation energy	meV	0	50	180	Measured over range of 0 to 100 $^{\circ}\text{C}$
Operating temp.	$^{\circ}\text{C}$	20	35	45	Annealed at 80 $^{\circ}\text{C}$ for 48 h
Pin layout	-				2 pin plug
Design of element	-				Silicon planar
Film thickness	μm	2	10	20	Approximate
Rise time constant	s		10		Odour-related
Decay time constant	s		10		Odour-related
Thermal conductivity ⁶	W/m/K	0.7	1	1.8	Over 7 to 67 $^{\circ}\text{C}$
Heat capacity ⁷	J/g/K	0.8	1.1	1.5	Over 7 to 67 $^{\circ}\text{C}$

which shows a gold, U-shaped layer 10 on the wafer 12. A substantially square deposition of polymer film 14 is shown centrally of the bridge 16 between the two arms 18 of the U-shape while electrode contact pads 20 are provided one at each free end of the arms 18. The polymer film square 14 may have dimensions a,b of 10 to 1000 μm square with an electrode gap c across which the polymer is grown of 0.1 to 1000 μm . The electrode contact pads may be 50 to 250 μm square d. The gold electrode structures were cleaned directly before deposition of the polymer films by cycling the potential between -0.30 and +1.80 V in 2 mol.dm⁻³ sulphuric acid at 100mVs⁻¹. The deposited polymer films were baked for 48 hours at 80°C in clean air after deposition to improve stability.

Poly(aniline) with butanesulphonate counterion. Films were grown from a solution containing 0.20 cm³ of aniline (0.4 mol dm⁻³) (Aldrich 99.5+%, purified by passing down a column of activated alumina) and 0.5cm³ of concentrated sulphuric acid (Fisons 98%) in 5 cm³ of a 0.5 mol dm⁻³ aqueous solution of sodium butanesulphonate (Fisons HPLC grade). The pH of the resulting solution, prior to polymer deposition, was approximately zero. Polymer films were deposited at room temperature under potentiostatic control by stepping the potential from 0.0 to +0.90 V vs. SCE for 10 s to nucleate the polymer and encourage even film growth, followed by stepping the potential to +0.78 V and holding for 110 s. After deposition the coated devices were thoroughly washed with reagent grade water and allowed to dry. The deposited polymer films were

baked for 48 hours at 80°C in clean air after deposition to improve stability.

Resistances were 6.0 ± 1.8 ohms ($n=6$).

Poly(aniline) with pentanesulphonate counterion. Films were grown from a
5 solution containing 0.20 cm³ of aniline (0.4 mol dm⁻³) (Aldrich 99.5+%, purified
by passing down a column of activated alumina) and 0.5cm³
of concentrated sulphuric acid (Fisons 98%) in 5 cm³ of a 0.5 mol dm⁻³ aqueous
solution of sodium pentanesulphonate (Fisons HPLC grade). The pH of the
resulting solution, prior to polymer deposition, was approximately zero. Polymer
10 films were deposited at room temperature under potentiostatic control by stepping
the potential from 0.0 to +0.90 V vs. SCE for 10 s to nucleate the polymer and
encourage even film growth, followed by stepping the potential to +0.78 V and
holding for 110 s. After deposition the coated devices were thoroughly washed
with reagent grade water and allowed to dry. The deposited polymer films were
15 baked for 48 hours at 80°C in clean air after deposition to improve stability.
Resistances were 4.8 ± 0.6 ohms ($n=3$).

Poly(aniline) with hexanesulphonate counterion. Films were grown from a
solution containing 0.20 cm³ of aniline (0.4 mol dm⁻³) (Aldrich 99.5+%, purified
20 by passing down a column of activated alumina) and 0.5cm³
of concentrated sulphuric acid (Fisons 98%) in 5 cm³ of a 0.5 mol dm⁻³ aqueous
solution of sodium hexanesulphonate (Fisons HPLC grade). The pH of the

resulting solution, prior to polymer deposition, was approximately zero. Polymer films were deposited at room temperature under potentiostatic control by stepping the potential from 0.0 to +0.90 V vs. SCE for 10 s to nucleate the polymer and encourage even film growth, followed by stepping the potential to +0.78 V and holding for 110 s. After deposition the coated devices were thoroughly washed with reagent grade water and allowed to dry. The deposited polymer films were baked for 48 hours at 80°C in clean air after deposition to improve stability. Resistances were 3.8 ± 0.1 ohms ($n=3$).

Poly(aniline) with heptanesulphonate counterion. Films were grown from a solution containing 0.20 cm³ of aniline (0.4 mol dm⁻³) (Aldrich 99.5+%, purified by passing down a column of activated alumina) and 0.5cm³ of concentrated sulphuric acid (Fisons 98%) in 5 cm³ of a 0.5 mol dm⁻³ aqueous solution of sodium heptanesulphonate (Fisons HPLC grade). The pH of the resulting solution, prior to polymer deposition, was approximately zero. Polymer films were deposited at room temperature under potentiostatic control by stepping the potential from 0.0 to +0.90 V vs. SCE for 10 s to nucleate the polymer and encourage even film growth, followed by stepping the potential to +0.78 V and holding for 110 s. After deposition the coated devices were thoroughly washed with reagent grade water and allowed to dry. The deposited polymer films were baked for 48 hours at 80°C in clean air after deposition to improve stability. Resistances were 4.1 ± 0.1 ohms ($n=3$).

Poly(aniline) with octanesulphonate counterion. Films were grown from a solution containing 0.20 cm³ of aniline (0.4 mol dm⁻³) (Aldrich 99.5+%, purified by passing down a column of activated alumina) and 0.5cm³ of concentrated sulphuric acid (Fisons 98%) in 5 cm³ of a 0.5 mol dm⁻³ aqueous solution of sodium octanesulphonate (Fisons HPLC grade). The pH of the resulting solution, prior to polymer deposition, was approximately zero. Polymer films were deposited at room temperature under potentiostatic control by stepping the potential from 0.0 to +0.90 V vs. SCE for 10 s to nucleate the polymer and encourage even film growth, followed by stepping the potential to +0.78 V and holding for 110 s. After deposition the coated devices were thoroughly washed with reagent grade water and allowed to dry. The deposited polymer films were baked for 48 hours at 80°C in clean air after deposition to improve stability. Resistances were 3.8 ± 0.4 ohms (n=5).

Poly(aniline) with nonanesulphonate counterion. Films were grown from a solution containing 0.20 cm³ of aniline (0.4 mol dm⁻³) (Aldrich 99.5+%, purified by passing down a column of activated alumina) and 0.5cm³ of concentrated sulphuric acid (Fisons 98%) in 5 cm³ of a 0.5 mol dm⁻³ aqueous solution of sodium nonanesulphonate (Fisons HPLC grade). The pH of the resulting solution, prior to polymer deposition, was approximately zero. Polymer films were deposited at 40°C under potentiostatic control by stepping the potential from 0.0 to +0.90 V vs. SCE for 10 s to nucleate polymer and encourage even

film growth, followed by stepping the potential to +0.78 V and holding for 110 s.

After deposition the coated devices were thoroughly washed with reagent grade water and allowed to dry. The deposited polymer films were baked for 48 hours at 80°C in clean air after deposition to improve stability. Resistances were 3.6 ± 0.5

5 ohms (n=10).

Poly(aniline) with decanesulphonate counterion. Films were grown from a solution containing 0.20 cm³ of aniline (0.4 mol dm⁻³) (Aldrich 99.5+%, purified by passing down a column of activated alumina) and 0.5cm³

10 of concentrated sulphuric acid (Fisons 98%) in 5 cm³ of a 0.5 mol dm⁻² aqueous solution of sodium decanesulphonate (Fisons HPLC grade). The pH of the resulting solution, prior to polymer deposition, was approximately zero. Polymer films were deposited at 40°C under potentiostatic control by stepping the potential from 0.0 to +0.90 V vs. SCE for 10 s to nucleate the polymer and encourage even

15 film growth, followed by stepping the potential to +0.78 V and holding for 110 s.

After deposition the coated devices were thoroughly washed with reagent grade water and allowed to dry. The deposited polymer films were baked for 48 hours at 80°C in clean air after deposition to improve stability. Resistances were 3.3 ± 0.1 ohms (n=3).

20

Poly(aniline) with (1R)-(-)-10-camphorsulphonate or (1S)-(+)-10-

camphorsulphonate counterion. Films were grown from a solution containing 0.20

cm³ of aniline (0.4 mol dm⁻³) (Aldrich 99.5+%, purified by passing down a column of activated alumina) in 5 cm³ of a 1.0 mol dm⁻³ aqueous solution of (1R)-(-)-10-camphorsulphonic acid (Aldrich 98%) or (1S)-(+)-10-camphorsulphonic acid (Aldrich 99%). The pH of the resulting solution, prior to polymer deposition, was approximately 0.25. Polymer films were deposited at room temperature under potentiostatic control by stepping the potential from 0.0 to +0.90 V vs. SCE for 120 s. After deposition the coated devices were thoroughly washed with reagent grade water and allowed to dry. The deposited polymer films were baked for 48 hours at 80°C in clean air after deposition to improve stability. Resistances were 8.5 ± 2.0 ohms (n=5) and 11.3 ± 2.1 ohms (n=4) respectively.

Poly(aniline) with (±)-10-camphorsulphonate counterion.

Films were grown from a solution containing 0.20 cm³ of aniline (0.4 mol dm⁻³) (Aldrich 99.5+%, purified by passing down a column of activated alumina) in 5 cm³ of a 1.0 mol dm⁻³ aqueous solution of (±)-10-camphorsulphonic acid (Aldrich 98, 99%). The pH of the resulting solution, prior to polymer deposition, was approximately 0.25. Polymer films were deposited at room temperature under potentiostatic control by stepping the potential from 0.0 to +0.90 V vs. SCE for 120 s. After deposition the coated devices were thoroughly washed with reagent grade water and allowed to dry. The deposited polymer films were baked for 48 hours at 80°C in clean air after deposition to improve stability. Resistances were 13.9 ± 7.2 ohms (n=7).

Poly(pyrrole) with (1R)-(-)-10-camphorsulphonate or (1S)-(+)-10-

camphorsulphonate counterion. Films were grown from a solution containing 0.1 mol dm⁻³ pyrrole (Aldrich 99.5+%, purified by passing down a column of activated alumina) 1.0 mol dm⁻³ (1R)-(-)-10-camphorsulphonic acid (Aldrich 98%) or (1S)-
5 (+)-10-camphorsulphonic acid (Aldrich 99%). Polymer films were deposited at room temperature under potentiostatic control by stepping the potential from 0.0 to +0.75 V vs. SCE for 120 s. After deposition the coated devices were thoroughly washed with reagent grade water and allowed to dry. The deposited polymer films were baked for 48 hours at 80°C in clean air after deposition to improve stability.

10 Resistances were 13.6 ± 4.1 ohms (n=5) and 9.6 ± 2.6 ohms (n=6) respectively.

Poly(pyrrole) with (±)-10-camphorsulphonate counterion. Films were grown from a solution containing 0.1 mol dm⁻³ pyrrole (Aldrich 99.5+%, purified by passing down a column of activated alumina) 1.0 mol dm⁻³ (±)-10-camphorsulphonic acid
15 (Aldrich 98, 99%). Polymer films were deposited at room temperature under potentiostatic control by stepping the potential from 0.0 to +0.75 V vs. SCE for 120 s. After deposition the coated devices were thoroughly washed with reagent grade water and allowed to dry. The deposited polymer films were baked for 48 hours at 80°C in clean air after deposition to improve stability. Resistances were

20 13.7 ± 1.8 ohms (n=5).

Poly(pyrrole) with copper (II) phthalocyaninetetrakisulphonate counterion. Films

were grown from a solution containing 0.1 mol dm^{-3} pyrrole (Aldrich 99.5+%, purified by passing down a column of activated alumina) 1.0 mol dm^{-3} aqueous solution of sodium copper (II) phthalocyaninetetrasulphonate (Aldrich). Polymer films were deposited at room temperature under potentiostatic control by stepping the potential from 0.0 to +0.80 V vs. SCE for 120 s. After deposition the coated devices were thoroughly washed with reagent grade water and allowed to dry. The deposited polymer films were baked for 48 hours at 80°C in clean air after deposition to improve stability. Resistances were $13.7 \pm 1.8 \text{ ohms}$ ($n=5$).

10 Alkane Phosphonate Counterions

Polypyrrole films were also grown with a range of alkanephosphonate counterions: Methane, ethane, butane and decane phosphonic acids are commercially available, the other members of the preferred series are not. Pentane and hexane phosphonic acids were synthesised by the Arbusov reaction (Kosolapoff, G. M., J. Amer. Chem. Soc., 66 (1944)109-111; Kosolapoff, G. M., J. Amer. Chem. Soc., 67 (1945)1180-1182) to give the corresponding ethyl esters followed by acid hydrolysis. Heptane, octane, nonane and undecane phosphonic acids were synthesised by the Michaels-Becker reaction (Ford-Moore, A.H., Howarth Williams, J., J. Chem. Soc., (1947)1465-1467) to give the corresponding butyl esters followed by acid hydrolysis.

Poly(pyrrole) with methanephosphonate counterion. Films were grown from a

solution containing 0.1 mol dm^{-3} pyrrole (Aldrich 99.5+%, purified by passing down a column of activated alumina) 1.0 mol dm^{-3} aqueous solution of methanephosphonic acid (Lancaster Synthesis). Polymer films were deposited at 20°C under potentiostatic control by stepping the potential from 0.0 to +0.70 V vs. SCE for 120 s. After deposition the coated devices were thoroughly washed with reagent grade water and allowed to dry. The deposited polymer films were baked for 48 hours at 80°C in clean air after deposition to improve stability.

Poly(pyrrole) with ethanephosphonate counterion. Films were grown from a solution containing 0.1 mol dm^{-3} pyrrole (Aldrich 99.5+%, purified by passing down a column of activated alumina) 1.0 mol dm^{-3} aqueous solution of ethanephosphonic acid (Lancaster Synthesis). Polymer films were deposited at 20°C under potentiostatic control by stepping the potential from 0.0 to +0.70 V vs. SCE for 120 s. After deposition the coated devices were thoroughly washed with reagent grade water and allowed to dry. The deposited polymer films were baked for 48 hours at 80°C in clean air after deposition to improve stability.

Poly(pyrrole) with butanephosphonate counterion. Films were grown from a solution containing 0.1 mol dm^{-3} pyrrole (Aldrich 99.5+%, purified by passing down a column of activated alumina) 1.0 mol dm^{-3} aqueous solution of butanephosphonic acid (Lancaster Synthesis). Polymer films were deposited at 20°C under potentiostatic control by stepping the potential from 0.0 to +0.80 V vs.

SCE for 360 s. After deposition the coated devices were thoroughly washed with reagent grade water and allowed to dry. The deposited polymer films were baked for 48 hours at 80°C in clean air after deposition to improve stability. Resistances were $5.9 \pm 2.9 \text{ kohms}$ ($n=3$).

5

Poly(pyrrole) with decanephosphonate counterion. Films were grown from a solution containing 0.1 mol dm^{-3} pyrrole (Aldrich 99.5+%, purified by passing down a column of activated alumina) 1.0 mol dm^{-3} aqueous solution of decanephosphonic acid (Lancaster Synthesis). Polymer films were deposited at 10 30°C under potentiostatic control by stepping the potential from 0.0 to +1.00 V vs. SCE for 240 s. After deposition the coated devices were thoroughly washed with reagent grade water and allowed to dry. The deposited polymer films were baked for 48 hours at 80°C in clean air after deposition to improve stability. Resistances were $1.3 \pm 0.9 \text{ kohms}$ ($n=4$).

15

The experiments using butane phosphonate and decanephosphonate were repeated using the same conditions but using pentane, hexane, heptane, octane, nonane and undecane phosphonic acids. In each case the concentration of the acid was either 0.1 mol dm^{-3} or 0.05 mol dm^{-3} . Table 1 summarises the resistance data for 20 polypyrrole films grown with the different alkane phosphonate counterions for a fixed growth potential (Eg).

The general results are shown in the appended table 2 and graphs. It is seen that the polymers behave as heavily doped p-type semiconductors. The figures from the appended table for resistance in air illustrate that the base line resistance is sensitive to humidity. It is observed that the polymers' resistance in odour is dependent upon humidity and indeed the polymers can have a high sensitivity to water vapour. The graph of activation energy against chain length provides a measure of the temperature sensitivity of the polymers. The friction co-efficient and wear rate of the poly(pyrolle) polymer films is seen to be good.

10 SILANIZATION OF SILICON SUBSTRATES

Gas sensor substrates were baked at 180°C for 15 hours. The devices were then cleaned by immersing in dichloromethane (Fisons >99%) for 40 minutes followed by immersion in 2mol.dm⁻³ H₂SO₄/HNO₃ for 40 minutes.

15 The devices were then washed with water and dried overnight at 60°C.

To silanize the devices, they were immersed in 20-30mmol⁻³ solution of octyltrichlorosilane (Aldrich 97%) in hexadecane (Aldrich 99+%) under Argon for 4-24 hours.

20

The devices were washed with pure hexadecane followed by dichloromethane and baked at 180°C for 1.5 hours. The devices were then rinsed with ethanol followed

by water.

A conducting polymer such as described in the preceding pages may then be grown on the substrate in the manner described in the applicant's co-pending International patent application no. PCT/GB95/00090. The polymer grows directionally and hence a thinner sensor layer can be deposited between electrodes. In addition, the technique enables wider electrode gaps to be bridged than previously enabling the resistance of the device to be increased and hence its sensitivity without increasing the response time. In addition the ability to deposit films across wider gaps allows the design of more sophisticated structures using a range of electrode spacings. A further benefit of this approach is that it allows a wider range of polymers to be used including those which will not grow successfully across unmodified gaps of moderate size (5-20 micron) such as poly(N-methylpyrrole) grown with tosylate counterions.

CLAIMS

1. A conducting polymer film comprising a polymer and an organosulphonate and/or an organophosphonate counterion.

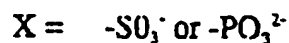
5 2. A conducting polymer film according to claim 1, wherein the polymer is poly(aniline) or poly (pyrrole).

3. A conducting polymer film according to claims 1 or 2, wherein the counterion is represented by the formula:

10



where: R = a C₁ to C₁₀ straight, branched cyclic or polycyclic, alkyl or keroalkyl group or organometallic group



15

$$n = 1-4$$

4. A conducting polymer film according to claim 3, wherein R is a C₁ to C₁₀ straight chain alkyl, an isomer of camphor or Copper II phthalocyanine.

20

5. A conducting polymer film according to any previous claim comprising poly(aniline) with butanesulphonate, pentanesulphonate, hexanesulphonate.

heptanesulphonate, octanesulphonate, nonanesulphonate, decanesulphonate, (1R)-(-)-10- camphorsulphonate, or (\pm)-10- camphorsulphonate counterions.

6. A conducting polymer film according to claims 1 to 4 comprising
5 poly(pyrrole) with methanephosphonate, ethanephosphonate, butanephosphonate, decanephosphonate, (1R)-(-)-10 camphorsulphonate, (1S)-(+)-10- camphorsulphonate, or (\pm)-10-camphorsulphonate or copper (II) phthalocyaninetetrasulphonate counterions.

10 7. A conducting polymer film according to claim 6, wherein the poly(pyrrole) is poly(N-methylpyrrole).

8. A conducting polymer film according to any previous claim deposited onto a gold, platinum, carbon, tin oxide, copper or doped silicon electrode.

15

9. A conducting polymer film according to any previous claim for use in a sensing device.

20

10. A conducting polymer film according to any previous claim for use in friction reduction.

11. A method of producing a conducting polymer film according to any

previous claim.

12. A method according to claim 11, wherein the polymer film is deposited above room temperature.

5

13. A method according to claim 12, wherein the polymer film is deposited at a temperature between 50°C and 55°C.

10

14. A method according to claims 11 to 13 wherein the deposited film is heat treated at a temperature which is higher than the deposition temperature.

15. A method of electrochemically producing a thin conductive polymer film on a substrate comprising the step of silanizing the substrate.

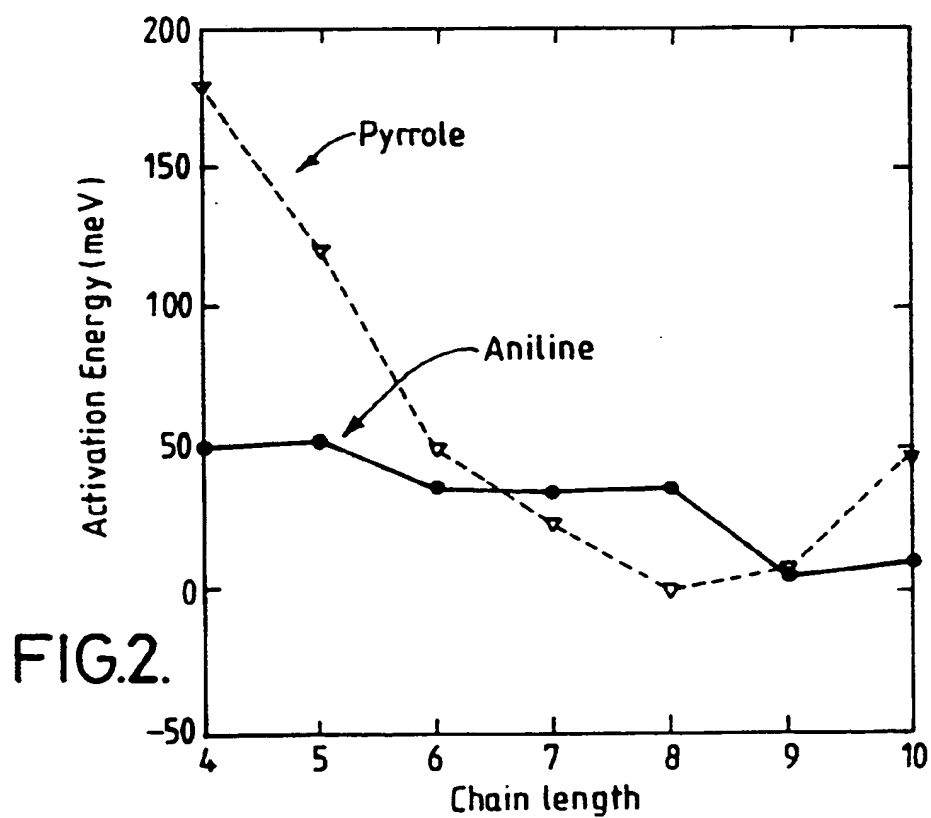
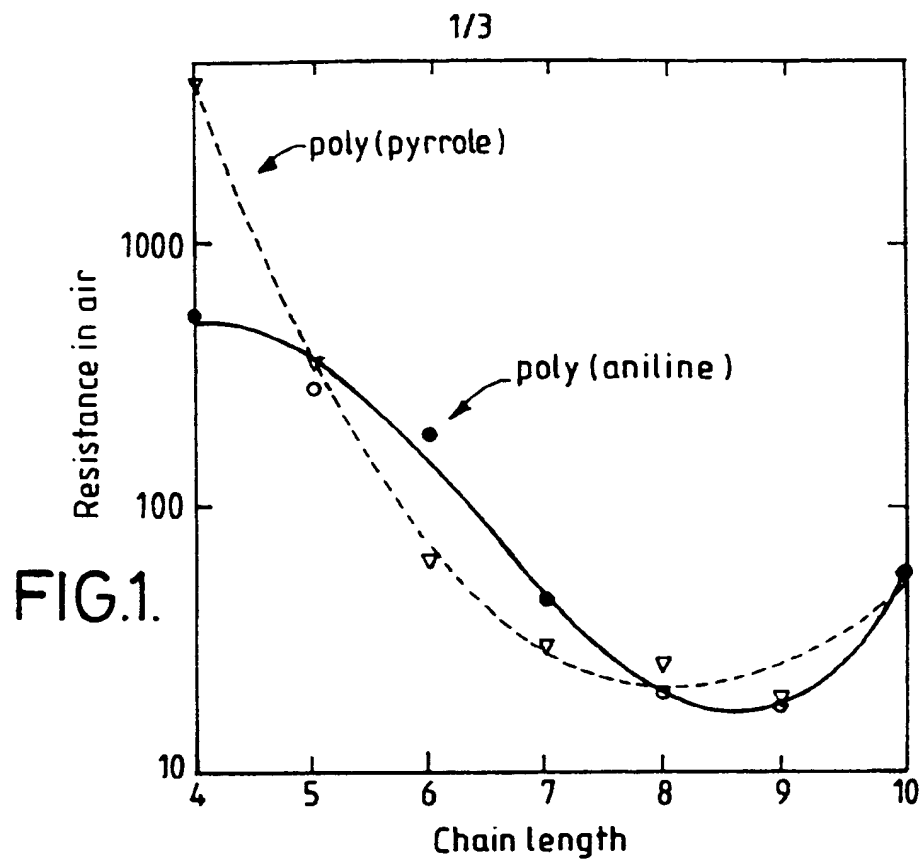
15

16. A method according to claim 15, wherein the substrate is silicon.

17. A method according to claims 15 or 16, wherein the agent used to silanize the substrate is an n-alkylisane.

20

18. A method according to claims 15 to 17 wherein the thin conductive polymer film is a thin conductive polymer according to claims 1 to 10.



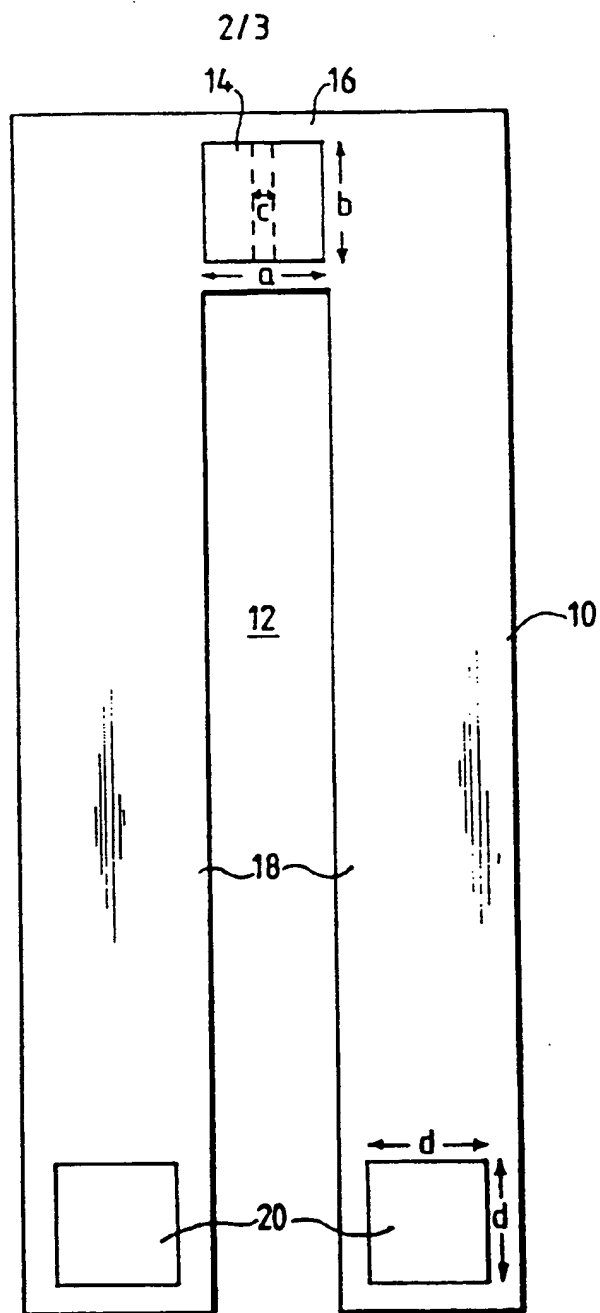


FIG.3.

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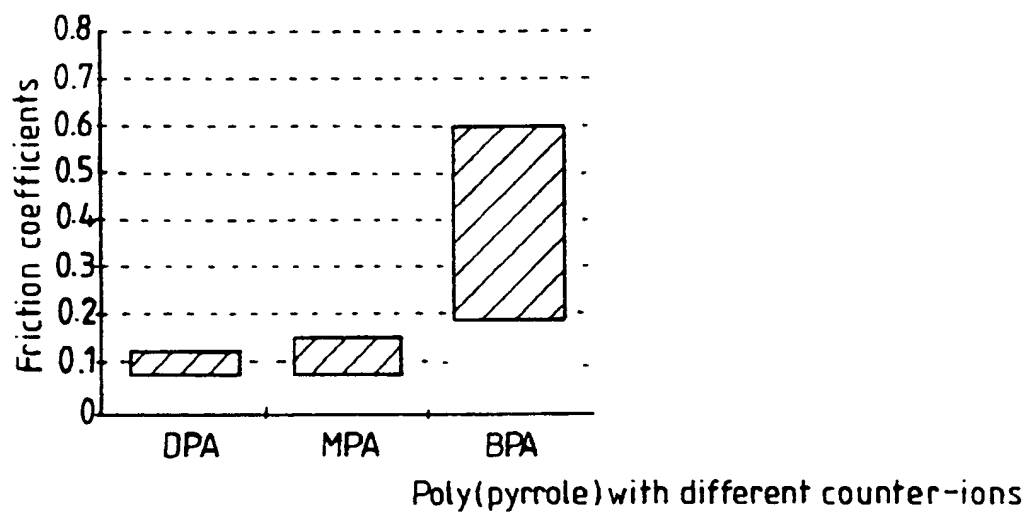
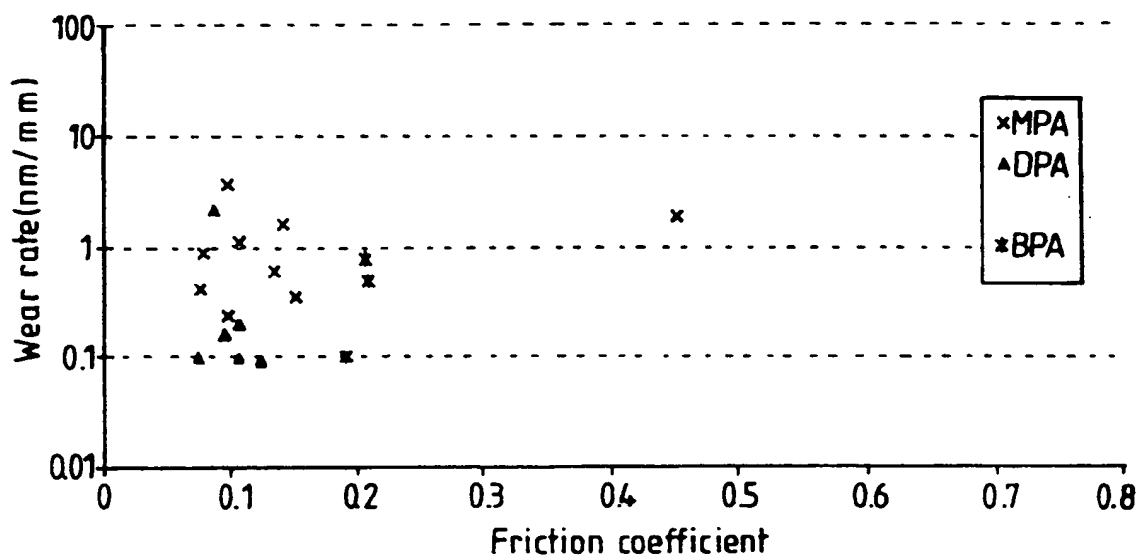


FIG.4.



MBA-methanephosphonate

DPA-decanephosphonate

BPA-butanephosphonate

FIG.5.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 96/01724

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 H01B1/12 C08G73/02 C25B3/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H01B C08G C25B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO,A,95 19458 (UNIVERSITY OF WARWICK) 20 July 1995 cited in the application see page 2, line 18 - page 3, line 3 see page 10, line 21 - page 11, line 7 see page 13, line 20 - page 14, line 5 ---	1-11
P,X	WO,A,96 22317 (KOREA INSTITUTE OF SCIENCE AND TECHNOLOGY) 25 July 1996 see the whole document --- -/-	1-3



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Date of the actual completion of the international search

4 November 1996

Date of mailing of the international search report

19. 11. 96

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 96/01724

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE WPI Section Ch, Week 9416 Derwent Publications Ltd., London, GB; Class A85, AN 94-128641 XP002017553 & JP,A,06 069 082 (NEC CORP) , 11 March 1994 see abstract</p>	1-5
X	<p>--- WO,A,89 01694 (ALLIED-SIGNAL) 23 February 1989 see claims 1-36</p>	1-4
X	<p>--- WO,A,92 18988 (ALLIED SIGNAL) 29 October 1992 see the whole document</p>	1-5
X	<p>--- WO,A,93 05519 (ALLIED-SIGNAL) 18 March 1993 see the whole document</p>	1-6
X	<p>--- EP,A,0 413 382 (SOLVAY) 20 February 1991 see the whole document</p>	1-4,6
X	<p>--- EP,A,0 191 726 (CIBA-GEIGY) 20 August 1986 see the whole document -----</p>	1-4,6

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 96/01724

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9519458	20-07-95	AU-A- 1422495	01-08-95
WO-A-9622317	25-07-96	NONE	
WO-A-8901694	23-02-89	US-A- 5069820	03-12-91
		CA-A- 1337366	17-10-95
		DE-D- 3852546	02-02-95
		DE-T- 3852546	11-05-95
		EP-A- 0380517	08-08-90
		JP-T- 3501264	22-03-91
		US-A- 5456862	10-10-95
		US-A- 5160457	03-11-92
		US-A- 5378403	03-01-95
WO-A-9218988	29-10-92	US-A- 5281363	25-01-94
		EP-A- 0581898	09-02-94
		JP-T- 6506977	04-08-94
		US-A- 5378404	03-01-95
WO-A-9305519	18-03-93	EP-A- 0601105	15-06-94
		JP-T- 6510555	24-11-94
		US-A- 5378404	03-01-95
EP-A-413382	20-02-91	FR-A- 2650909	15-02-91
		AT-T- 132658	15-01-96
		DE-D- 69024559	15-02-96
		DE-T- 69024559	05-09-96
		JP-A- 3179715	05-08-91
		US-A- 5284723	08-02-94
EP-A-191726	20-08-86	JP-A- 61168651	30-07-86
		US-A- 4771111	13-09-88